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CITATION:

SHIRAISHI, Soshi ...[et al]. Electric double layer capacitance of activated carbon nanofibers in ionic liquid: EMImBF. Electrochemistry 2007, 75(8): 619-621

ISSUE DATE:

2007-08-05

URL:

<http://hdl.handle.net/2433/245269>

RIGHT:

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Electric Double Layer Capacitance of Activated Carbon Nanofibers in Ionic Liquid : EMImBF₄

イオン液体中における活性化カーボンナノファイバの
電気二重層容量

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Abstract

The double layer capacitance of an activated carbon nanofiber (ACNF) with a 100~200 nm fiber-diameter, prepared by the polymer blend spinning technique, was investigated using 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) as the electrolyte. The conventional activated carbon fiber (ACF) with the fiber-diameter of ~ 10 μm and narrow micropores (~ 0.7 nm pore-width) showed a significant irreversible adsorption of EMIm⁺ cation in EMImBF₄, however, the ACNF effectively suppress the irreversibility even with the pore structure comparable to the conventional ACF. This suggests the effect of the short pass length on the ion adsorbing/desorbing process. The decreased capacitance by the cycling in EMImBF₄ was recovered by the addition of propylene carbonate as an organic solvent to the electrolyte. This means that the irreversible adsorbed ions can be desorbed using propylene carbonate.

Introduction

Recently, an ionic liquid, i.e., a room-temperature molten salt, has become very attractive as an electrolyte for the electric double layer capacitor (EDLC) due to its high chemical stability, high ionic conductivity, and non-flammable property [1,2]. Therefore, the capacitance behavior of activated carbons in an ionic liquid has been characterized and the following two characteristic points were recently determined. The first one is that a higher capacitance is observed in the 1-ethyl-3-methylimidazolium-based ionic liquid compared to the typical organic electrolyte for EDLC [3,4]. Watanabe, et al. proposed the influence of higher carrier concentration on the double layer structure of the carbon surface [3], but the details have not been clarified. The second one is that activated carbons with narrow micropores cause a drastic capacitance decline in the 1-ethyl-3-methylimidazolium-based ionic liquid [4]. For the propylene carbonate electrolyte, the activated carbons with narrow micropores such as $\sim 0.7\text{nm}$ showed a low capacitance due to strong ion sieving, but the capacitance cycling was stable. This capacitance decline in the ionic liquid might be due to the presence of an interaction between the imidazolium cation and the carbon micropore. Chen et al. reported that the narrow hollow in multi-walled carbon nanotube promotes the crystallization of 1-butyl-3-methylimidazolium hexafluorophosphate, which suggests the effect of nanospace on the physicochemical behavior of the ionic liquid [5]. This interaction can be expected to depend on the pore structure. In fact, our previous paper reported that mesoporous carbon black showed no capacitance decline in spite of only an $\sim 1000\text{ m}^2\text{g}^{-1}$ BET specific surface area [4]. Similarly, the short pore-length might suppress the capacitance decline.

Our group recently succeeded in preparing phenolic resin based-carbon nanofiber (CNF) by the polymer blend spinning technique [6,7]. This technique produces bundles of CNFs with a several hundred nm fiber-diameter. Furthermore, the resulting CNFs can be gasified by the traditional activation technique such as steam or CO₂ to form a well-developed micropore structure with a specific surface area of > 1000 m²g⁻¹ since the phenolic resin is a good precursor for activated carbon. The resulting activated carbon nanofiber (ACNF) should have shorter micropore-length because of a nano-sized fiber-diameter, compared with the conventional activated carbon fiber (ACF). Based on the difference in fiber length between the ACNF and the ACF, the micropore length of the ACNF can be considered to be around 1/100 of that of the ACF.

In the present report, we address the capacitance behavior in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) of the ACNF to clarify the effect of the short micropore length on suppressing the capacitance decline in EMImBF₄. EMImBF₄ is a good standard ionic liquid since BF₄⁻ anion is the most used anion for EDLC and the capacitance behavior of activated carbons in EMIm⁺ based ionic liquid has been investigated well [1,2,8].

Experimental

The original CNFs are prepared by the spinning and carbonization of a polymer blend composed of phenolic resin and polyethylene in the same manner as previously reported [6,7]. The CNFs were steam-activated to develop the micropores. The micropore structure was controlled by the activation duration. The BET specific surface area, pore volume, and mean micropore size were calculated from the nitrogen

adsorption isotherm at 77K [9]. The morphology of the ACNFs was observed by a field emission type scanning electron microscope (FE-SEM).

We used the EMImBF₄ synthesized by the direct reaction of EMIm(HF)_{2.3}F with BF₃ gas [10]. The water content of the EMImBF₄ was less than 150 ppm. A composite pellet electrode (diameter : 13 mm) was prepared from ground ACNF (0.05 g), acetylene black as the conductor, and the PTFE-binder. The ratio of the sample, acetylene black, and binder in the electrode was 80, 10, and 10 wt%, respectively. Al mesh (20 mm×40mm, 0.1t, LW:SW:W = 2:1:0.2, Thank-metal Co. Ltd., Japan) was used as the current collector for the composite electrode. The capacitance measurement was conducted by a galvanostatic method using a three-electrode system in the same way as the previous report [4]. The ACF corresponding to the sample “ACF-60” or “ACF120” in the previous report was also use as reference carbon materials for the electrochemical behavior. Additionally, the capacitance measurement in propylene carbonate (PC) solution containing EMImBF₄ as electrolyte salt was also carried out after the measurement in the pure EMImBF₄ to realize the recovery of the lost capacitance by the electrochemical operation in the EMImBF₄. The EMImBF₄ was dissolved in PC (Capacitor grade, Kishida Chemical, Co. Ltd., Japan) to prepare the PC solution containing 0.5 moldm⁻³ EMImBF₄ (0.5M EMImBF₄/PC). The electrode was transferred from the cell for the pure EMImBF₄ electrolyte to that for the 0.5M EMImBF₄/PC electrolyte after finishing the measurement in the pure EMImBF₄.

Results and discussion

The FE-SEM image (**Fig. 1**) showed that ACNF-3 is composed of a bundle of carbon nanofibers with 100~200 nm diameter. This fiber diameter is about 1% of the

conventional activated carbon fibers such as ACF60 or ACF120. The other ACNFs also show a morphology similar to ACNF-3. Table 1 shows the pore structure parameters of various ACNFs and ACFs. All the ACNFs were porous carbons with specific surface areas of $900 \sim 2000 \text{ m}^2\text{g}^{-1}$. The pore volume data (V_{meso} , V_{micro}) showed that ACNF-1 and ACNF-2 were microporous carbons, while ACNF-3 also had a comparable mesopore volume to the micropore. Yang et al. also succeeded in the preparation of the activated CNF using an electro-spinning method of the PAN polymer, but their BET specific surface area was not higher than $1200 \text{ m}^2\text{g}^{-1}$ [11]. The widely controllable pore-structure is a characteristic point of our activated CNF. Comparing ACNF-1 and ACF60, they basically had a comparable pore structure although the S_{BET} and V_{micro} values of ACNF-1 were slightly lower than those of ACF60. The mesopore volume of ACNF-1 was greater than that of ACF60, however, the N_2 adsorption isotherm and the pore size distribution curve in the mesopore region (data not shown) suggest that the mesoporosity of ACNF-1 is mainly related to the inter-space (nearly macropore region) between the fibers rather than the presence of mesopores in the carbon surface. The surface oxygen functionalities were also checked by X-ray photoelectron spectroscopy. The chemical state and the amount of the surface oxygen were very similar for ACNFs and ACFs. Therefore, ACNF-1 and ACF60 can be considered as good samples to investigate the effect of the fiber diameter on the capacitance.

Fig. 2 shows the chronopotentiograms of the first, second, and third cycles for the ACNFs. The potentiogram profiles of all the samples started around 3.2 V vs. Li/Li^+ , decreased to 2V vs. Li/Li^+ and then increased to 4V vs. Li/Li^+ . All the profiles were nearly straight lines, which kept constant gradients during the cycles. The

inverse of the profile gradient corresponds to the capacitance of the galvanostatic method [6]. Therefore, **Fig. 2** suggests that the capacitive behavior of these ACNFs is stable during the cycling and that the capacitance order is $\text{ACNF-3} > \text{ACNF-2} > \text{ACNF-1}$. According to our previous reports [4], ACF60 and ACF120 showed the serious capacitance decline at the initial cycle in EMImBF₄, compared to the other ACFs consisting of wider micropores. The decline of ACF60 was larger than that of ACF120. These suggest that the activated carbons with narrow micropores cause a significant irreversible ion-adsorption in EMImBF₄. However, ACNF-1 exhibited more stable cycling-performance, although it has a comparable or lower microporosity to ACF60 as shown in Table 1.

The cycle dependence of the capacitance for the ACNFs and the ACFs is shown in **Fig. 3**. ACNF-2 and ACNF-3 showed constant capacitances during the 20 cycles in EMImBF₄. The capacitance of ACNF-1 gradually decreased with the increasing cycle numbers, but the decrease was not more significant than ACF60 and ACF120. ACNF-1 had a higher capacitance than ACF60. Moreover, ACNF-1 showed a higher capacitance at the 3rd cycle than ACF120 although the initial capacitance of ACNF-1 was lower than that of ACF120. This result suggests that the shorter pore length is effective for enhancing the capacitance and suppressing the capacitance decline in EMImBF₄. If the ion is moving in a short pore, the adsorbed ion in narrow micropore can be easily desorbed in the EMImBF₄.

Propylene carbonate (PC) is known to be a good solvent that dissolves EMImBF₄. Therefore, PC can be expected to release the immobile ions in the micropores during the cycling. The capacitances of ACNF-1 and ACF120 in 0.5M EMImBF₄/PC are also plotted in **Fig. 3**. The EMImBF₄/PC data was continuously

obtained using the same electrodes after the measurement in EMImBF₄. For both samples, the lost capacitance was recovered soon after using the EMImBF₄/PC, suggesting that the propylene carbonate breaks the interaction between the carbon micropore wall and EMIm⁺ cation.

Conclusion

The activated carbon nanofiber (ACNF), which was prepared by the polymer blend spinning technique, had a comparable microporosity to the conventional activated carbon fiber (ACF). The short micropore length of ACNF is effective in suppressing the significant capacitance decline caused by the cycling in EMImBF₄. The lost capacitances in EMImBF₄ for ACNF and ACF were recovered in the propylene carbonate electrolyte, suggesting that the irreversible adsorbed ions can be desorbed using propylene carbonate.

Acknowledgement

A part of this work was financially supported by a Grant-in-Aid for Scientific Research on Priority Area (Science of Ionic Liquids) and Young Scientist B in MEXT of Japan.

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Figure Captions

Figure 1 Field emission type scanning electron microscopic (FE-SEM) image of activated carbon nanofiber (ACNF-3).

Figure 2 Chronopotentiograms (potential-time curve at galvanostatic condition, 40 mA g^{-1} , $2 \sim 4 \text{ V}$ vs. Li/Li^+) of ACNF electrodes in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄).

Figure 3 Dependence of the capacitance (40 mA g^{-1} , $2 \rightarrow 4 \text{ V}$ vs. Li/Li^+) of ACNF and ACF electrodes on the cycle numbers in EMImBF₄ and propylene carbonate solution containing 0.5 M EMImBF_4 ($0.5 \text{ M EMImBF}_4 / \text{PC}$).

Table1 Pore structure parameters and electrode bulk density of ACNFs and ACF

Sample	S_{BET} [m ² g ⁻¹]	V_{meso} [mlg ⁻¹]	V_{micro} [mlg ⁻¹]	w_{micro} [nm]	d [gcm ⁻³]
ACNF-1	885	0.15	0.34	0.67	0.68
ACFN-2	1450	0.17	0.57	0.88	0.57
ACFN-3	2090	0.75	0.84	1.18	0.41
ACF60	970	0.06	0.37	0.66	0.87
ACF 120	1180	0.07	0.47	0.74	0.83

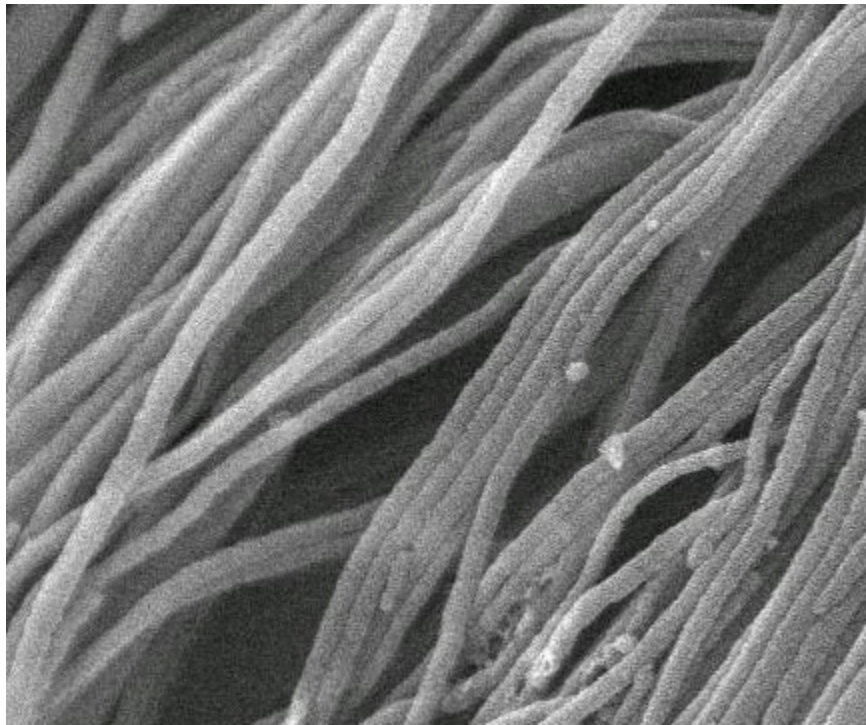
S_{BET} ; BET specific surface area.

V_{meso} ; mesopore (1.6~50nm) volume calculated by DH method.

V_{micro} ; micropore volume calculated by DR method.

w_{micro} ; mean micropore width calculated by DR method.

d ; bulk density of the composite electrode



1 μ m

Fig.1 S. Shiraishi, et al., Gunma University

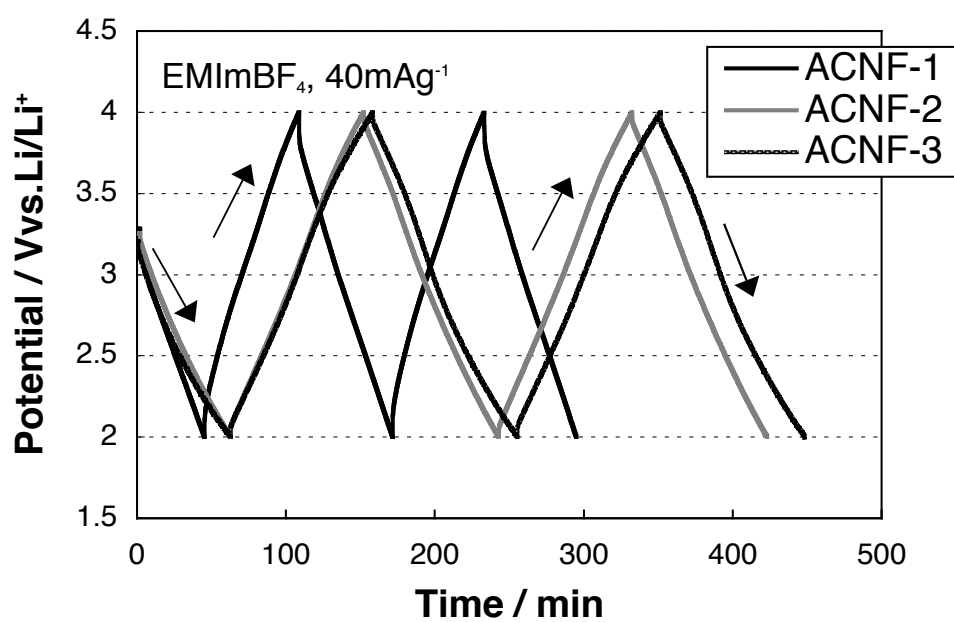


Fig.2 S. Shiraishi, et al., Gunma University

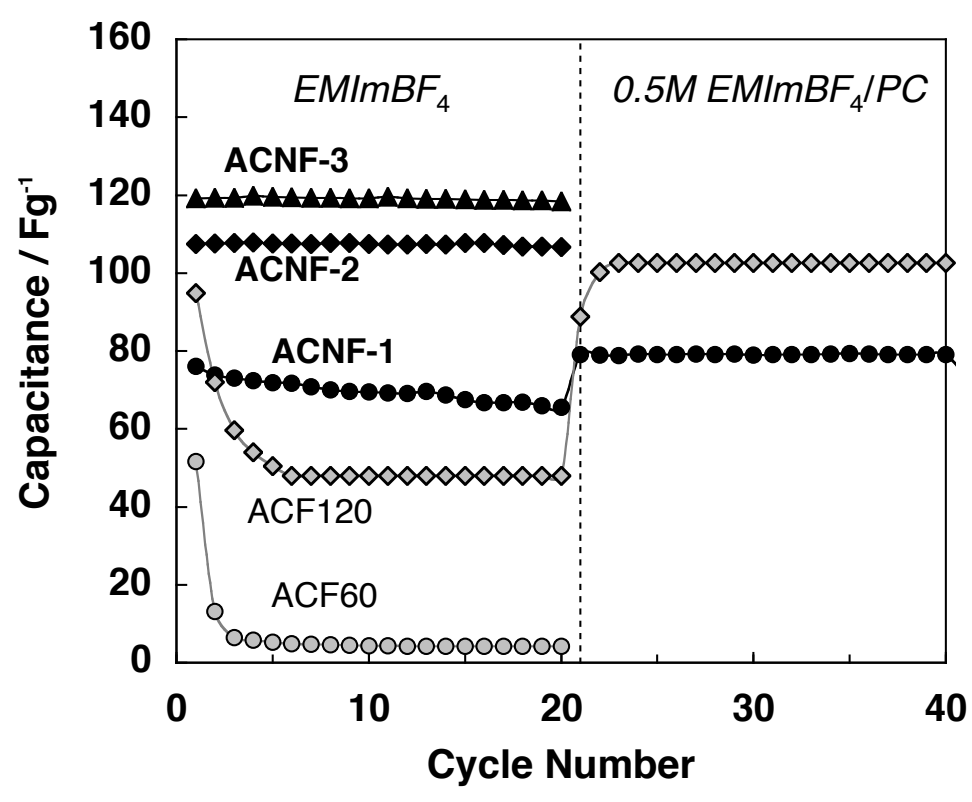


Fig.3 S. Shiraishi, et al., Gunma University